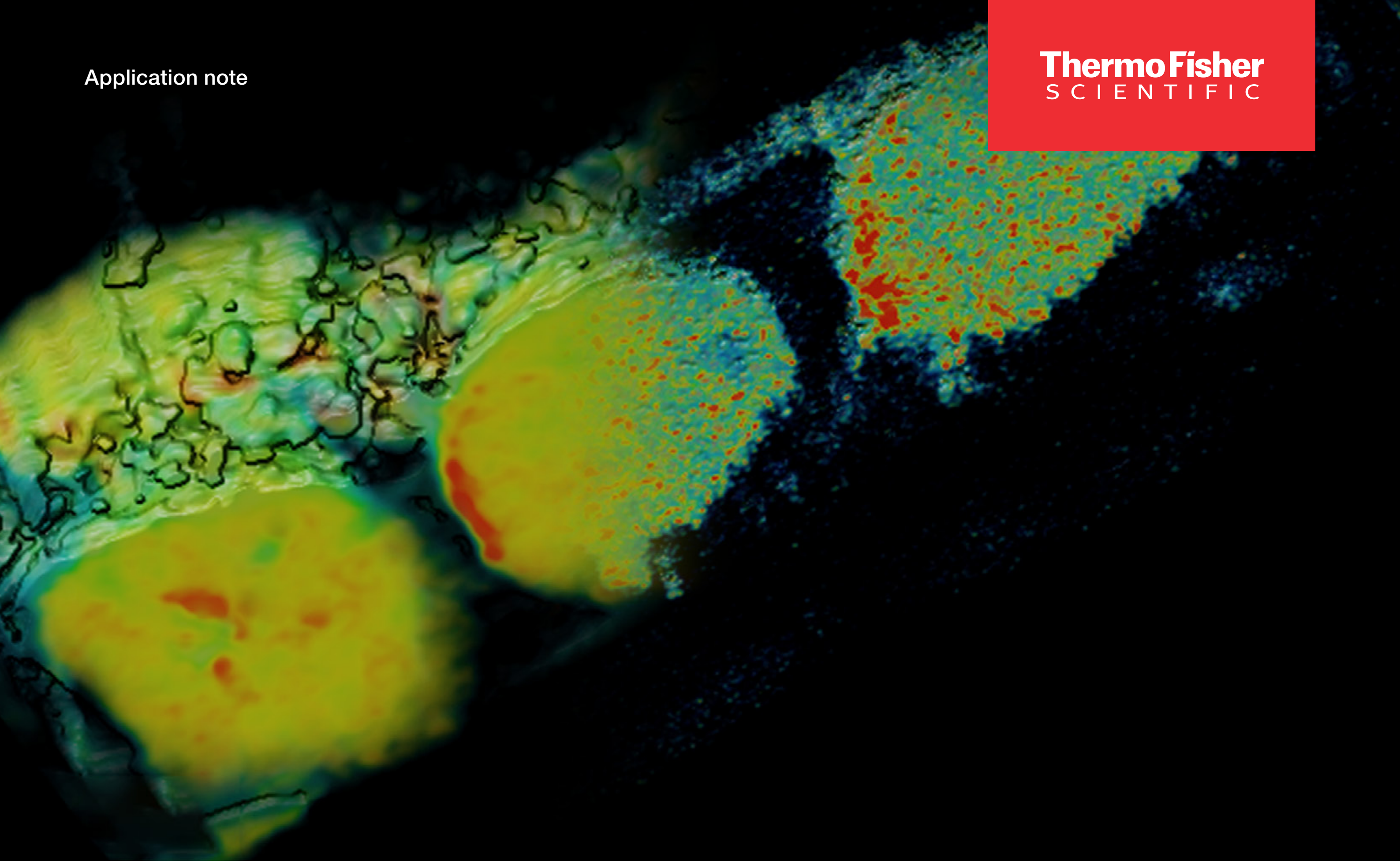
Application note



Enhanced 3D mapping of lithium ions in NMC811 using automated FIB and ToF-SIMS

Authors

Chengge Jiao, David Pacura, Peter Priecel, Patrick Barthelemy

Introduction

Optimized lithium-ion battery (LIB) performance is significantly influenced by the distribution of lithium ions (Li^+) within the cathode active material. While energy-dispersive X-ray spectroscopy (EDS) has been a primary technique for analyzing LIB cathode materials, it has difficulty detecting critical light elements like lithium and boron. Secondary-ion mass spectrometry (SIMS) is a powerful complementary technique with exceptional sensitivity for light elements, making it ideally suited for the characterization of Li^+ distribution in LIBs.

3D SIMS analysis of these materials must achieve optimal depth and lateral resolution. Conventional top-down SIMS depth profiling offers exceptional depth resolution for flat, multi-layered structures, but falls short in lateral resolution, particularly when dealing with the uneven surfaces commonly found on electrode active particle materials.

To address these challenges, this application note introduces a method that couples automated focused ion beam (FIB) cross-sectioning with time-of-flight SIMS (ToF-SIMS). By optimizing the process for both depth (z-resolution) and lateral (x, y) resolution, a comprehensive 3D map of the $^7Li^+$ distribution within NMC811 (lithium nickel manganese cobalt oxide) particles can be created.

PFIB cross-sectioning resolution

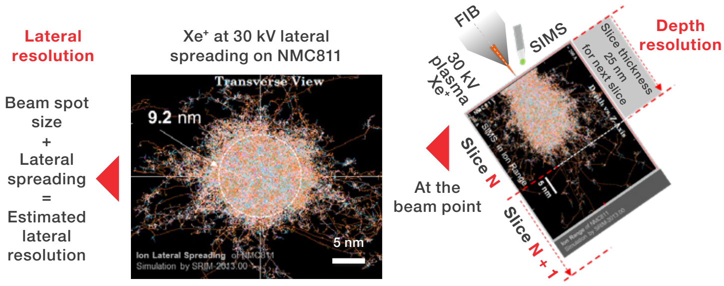


Figure 1. Diagram illustrating depth and lateral resolution in PFIB cross-sectioning. For NMC811 particles, a slice thickness of 25 nm offers a good compromise between adequate ion range depth for SIMS analysis and the collection of a sufficient number of particles for meaningful measurements.

Depth and lateral resolution are crucial factors that influence analysis quality. Lateral resolution is determined by the beam spot size and the ion beam spread within the material. Depth resolution is influenced by the ion range and slice thickness.

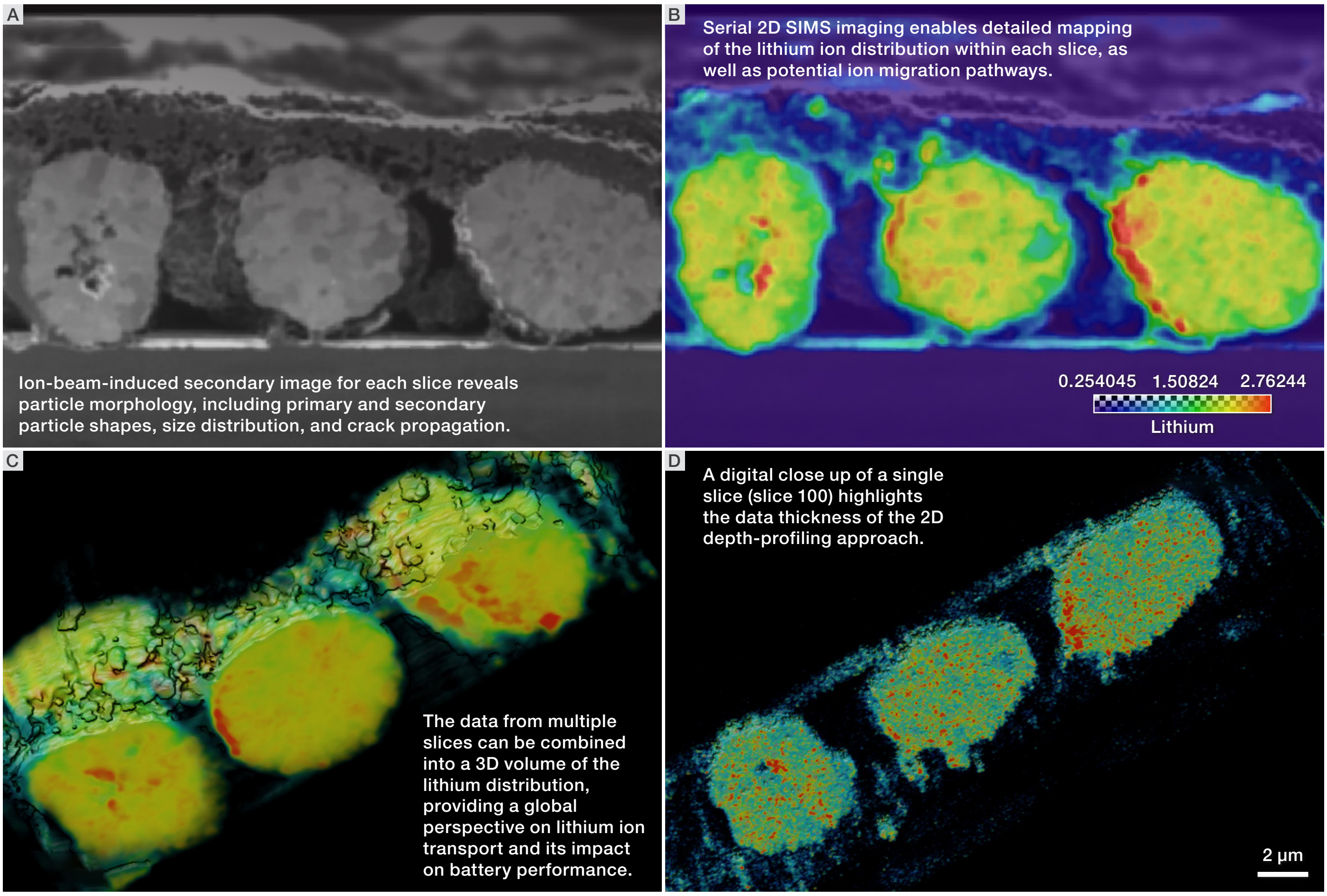


Figure 2. Automated FIB cross-sectioning, coupled with SIMS imaging, provides a comprehensive approach for the 3D, high-resolution analysis of lithium ion distribution in a pristine NMC811 electrode. This automated workflow is a powerful tool for the understanding of structure-property relationships in NMC811 particles and for the optimization of their performance.

Methodology

Sample preparation

Analyzed samples consisted of pristine NMC811 particles coated onto one side of an aluminum current collector. The sample was mounted on a pre-tilted stub with the current collector facing upwards; this mitigates milling curtains caused by the ion beam. As a typical gallium FIB can potentially react with lithium-containing materials, a Xe^+ plasma ion beam was used instead (termed plasma FIB, or PFIB).

Automated FIB cross-sectioning

A series of cross-sections was produced with the FIB for depth analysis. Cross-section slices had a thickness of 25 nm, closely matched to the primary beam ion stopping range at 30 kV. This approach offered a good balance between depth resolution and the maximum volume per slice during analysis. A rocking mill method was used to improve cross-section surface quality, ultimately enhancing lateral resolution while also using a low ion-beam current for SIMS data acquisition.

ToF-SIMS analysis

Thermo Scientific™ Auto Slice & View™ Software enables consistent, automated cross-sectioning with the FIB, which is facilitated further by a unique interface with seamless communication between the software and the ToF-SIMS. Once data collection is complete, the *.h5 spectrum files can be imported directly into Thermo Scientific™ Avizo™ Software for comprehensive data analysis.

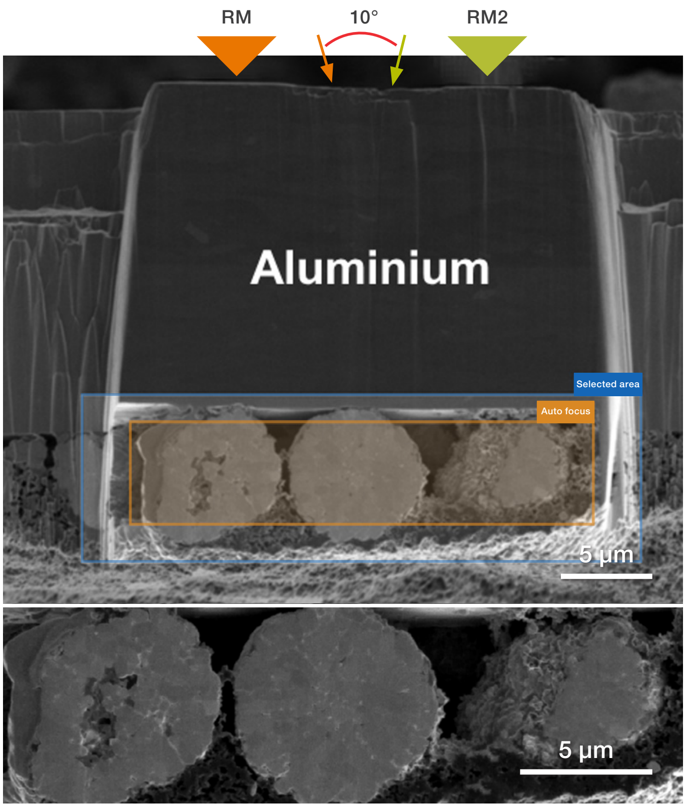


Figure 3. PFIB milling strategy for 3D SIMS data acquisition. Note that SIMS is a highly surface sensitive technique; if the cross-section has milling curtains, the SIMS signal will show vertical lines in the chemical map.

Results and discussion

The FIB/ToF-SIMS approach provides a combination of secondary electron and SIMS imaging, which is then aligned to produce a 3D representation of the lithium-7 distribution (Figure 2). Cross-sections, showing visible defects and internal cracks, can be seen directly within the FIB through the use of secondary electron micrographs (Figure 2A). 231 sections were collected in total at 30 pA, showing several ~5-6 µm diameter NMC particles. The signal intensity of the corresponding SIMS image (Figure 2B) reveals the distribution of $^{7}Li^{+}$ within the cross-section. Alignment and reconstruction in Avizo Software produces a 3D, full volume SIMS image of the $^{7}Li^{+}$ distribution throughout the NMC811 particles (Figure 2C).

These results demonstrate the effectiveness of 3D characterization with automated FIB cross-sectioning and ToF-SIMS. Particularly for the analysis of light elements, such as the lithium in battery electrode materials, this method provides several significant advantages:

- Efficient, rapid data acquisition thanks to the high ionization yield of $^{7}Li^{+}$
- Comprehensive analysis, as the milling process was able to encompass several NMC811 particles and even show their internal cracks
- Reliable system and stage positioning with Auto Slice & View Software, which remained stable throughout the 23-hour acquisition, and was capable of matching the rocking mill slicing at 15 nA to the SIMS data acquisition at 30 pA

Conclusions

3D SIMS is a powerful tool for the analysis of elemental and isotopic materials composition in three dimensions. The choice of 3D SIMS imaging approach depends on the nature of the sample (hardness, conductivity, etc.), the research goals, and the available instrumentation. For instance, if high depth resolution is required, FIB-SIMS depth profiling is often the preferred method. For larger sample areas, FIB slicing and SIMS imaging may be more suitable.

In this application note, the combined FIB/ToF-SIMS method was shown to overcome the limitations of conventional SIMS 3D depth profiling, especially when dealing with uneven surfaces. It provides valuable insights into the lithium distribution within electrode materials, offering a comprehensive understanding of the internal structure and composition of NMC811 particles.

References

1. Hovington, P, et al. Can we detect Li K X-ray in lithium compounds using energy dispersive spectroscopy? Scanning 38(6) p571-578 (2016). doi: 10.1002/sca.21302
2. Jiao, C, et al. Three-Dimensional Time-of-Flight Secondary Ion Mass Spectrometry and DualBeam FIB/SEM Imaging of Lithium-ion Battery Cathode. Microscopy and Microanalysis 25(S2) p876–877 (2019). doi: 10.1017/S1431927619005117

Learn more at **thermofisher.com/sims**